

# Atomic many-body effects and Lamb shifts in alkali metals

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We present a detailed study of the Flambaum-Ginges radiative potential method which enables the accurate inclusion of quantum electrodynamics (QED) radiative corrections in a simple manner in atoms, ions, and molecules over the range  $10 \leq Z \leq 120$ , where  $Z$  is the nuclear charge. Calculations are performed for binding energy shifts to the lowest valence  $s$ ,  $p$ , and  $d$  waves over the series of alkali atoms Na to E119. The high accuracy of the radiative potential method is demonstrated by comparison with rigorous QED calculations in frozen atomic potentials, with deviations on the level of 1%. The many-body effects of core relaxation and second- and higher-order perturbation theory on the interaction of the valence electron with the core are calculated. The inclusion of many-body effects tends to increase the size of the shifts, with the enhancement particularly significant for  $d$  waves; for K to E119, the self-energy shifts for  $d$  waves are only an order of magnitude smaller than the  $s$ -wave shifts. It is shown that account of many-body effects is essential for an accurate description of the Lamb shift.

## I. INTRODUCTION

The increasingly accurate account of electron-electron correlations in calculations of the properties of many-electron atoms, ions, and molecules has seen the need for quantum electrodynamics (QED) radiative corrections to be included in the formalism. The account of combined many-body effects and radiative corrections was crucial in the atomic theory interpretation of the cesium parity violation measurement [1], restoring an apparent deviation from the standard model of particle physics [2–9]. Tests of quantum electrodynamics in the measurements of transition frequencies in highly-charged many-electron ions also rely on an accurate description of combined many-body and QED effects (see, e.g., [10, 11]). The increasing size of the radiative corrections with nuclear charge  $Z$  makes the account of such effects necessary in the accurate prediction of the physical and chemical properties of the superheavy elements [12].

The methods of rigorous (“exact”) QED that have had such great success in applications for single- or few-electron atoms and ions are not tractable for the many-electron system [13]. While it is possible to determine QED corrections to atomic properties in the exact formalism in *frozen* atomic potentials (see, e.g., Refs. [14, 15] for Lamb shifts to binding energies in alkali atoms), in this approach important many-body effects such as core relaxation and electron-electron correlations may be prohibitively difficult to calculate.

The Lamb shift is the physical radiative shift which is comprised, in the one-loop approximation, of the non-local self-energy and the local vacuum polarization shifts, the former giving the larger effect. A number of approaches for estimating the Lamb shifts in many-electron atoms in a simple manner have been put forward, and we refer the reader to Ref. [16] for one such method and a description of earlier methods. Some approaches rely on rescaling the shifts, e.g., from the vacuum polarization. Others involve the introduction of an approximate potential, which we term a “radiative potential”, that

mimics the self-energy effects. These potentials are found by fitting to the self-energy shifts for hydrogen-like ions. A local radiative potential is appealing due to the ease in which it may be included into many-body atomic or molecular computer codes with the resulting full account of many-body effects.

We introduced such a local radiative potential a decade ago in our work Ref. [8]. This potential has been implemented in a number of calculations, including in the calculation of the parity violating amplitude in Cs [8] and other atoms and ions [17], in the spectra of heavy and superheavy atoms [18–20], and in highly-charged ions [21]. It has also been applied in Ref. [22] with slightly different fitting factors for the high-frequency part of the electric potential with fitting to hydrogen-like  $s$  waves for principal quantum number  $n = 1$  to  $n = 5$ .

Recent applications of other approaches include implementation [23] of a method based on Welton’s idea [24, 25]. See also Ref. [26–28] for the development and application of non-local radiative potentials.

Shabaev, Tupitsyn, and Yerokhin have demonstrated the very high accuracy of their non-local QED potential [27, 29], termed the “model operator”, by comparing their results for self-energy shifts with those of exact QED [15] performed in the same frozen atomic potentials. In their work, they hinted that the property of the non-locality of the self-energy should be preserved for obtaining high accuracy. This was based on the isolation of a term of the form  $A_\kappa \exp(-r/\alpha)$ , fitted to reproduce self-energy shifts for hydrogen-like ions for the lowest level in each wave  $\kappa$ , where  $\alpha$  is the fine-structure constant. (Throughout the paper we use atomic units,  $\hbar = e = m = 1$ ,  $c = 1/\alpha$ .) It was shown that this local potential yields  $s$ -wave self-energy shifts for neutral alkali atoms with increasingly large deviations from the results of exact QED with increasing nuclear charge  $Z$ , the error for Fr amounting to about 30%.

In the current work we determine the  $s$ -wave self-energy shifts to binding energies in alkali atoms using the Flambaum-Ginges local radiative potential [8] in frozen

atomic potentials. We demonstrate that the accuracy of the radiative potential method is high, the deviations from the results of exact QED on the level of 1%, the error roughly double that of the model operator approach [27]. The simplicity of this potential (not much more complicated than the Uehling potential) makes its inclusion into many-body methods and codes straightforward.

The combined self-energy and many-body effects on the binding energies in neutral atoms have not been studied in detail before. In this work we consider the many-body mechanisms and effects of core relaxation and core-valence correlations on the self-energy shifts of the neutral alkali atoms. Consideration of such many-body effects is crucial for obtaining the correct magnitude and sign of the shift for waves with orbital angular momentum  $l > 0$ . We have introduced an  $l$ -dependence into the electric part of the radiative potential which enables the  $d$ -level shifts to be controlled and the overall accuracy of the potential improved. The many-body enhancement mechanisms that we have observed in this work for the self-energy are the same that we saw in our recent work on the vacuum polarization (Uehling) shifts [30].

## II. THE RADIATIVE POTENTIAL

The Flambaum-Ginges radiative potential (FGRP) is a local potential that approximates the one-loop self-energy and vacuum polarization effects on electron energies and orbitals and may be readily included in many-body atomic structure calculations. The derivation of this potential may be found in Ref. [8]. The self-energy part of the potential contains factors that are found by fitting to self-energy shifts for states of high principal quantum number for hydrogen-like ions. In the current paper, we focus on the self-energy aspect of the problem. We addressed in detail many-body effects on the dominant contribution to the vacuum polarization (the Uehling potential) in our recent paper [30].

The following arguments justify the use of local radiative potentials in neutral atoms: (i) the radiative QED interactions act at small distances, on the order of the Compton wavelength  $r \sim \alpha$ , where the electrons are unscreened by other electrons; (ii) the binding energies of valence electrons in neutral atoms are much smaller than the rest-mass energy,  $\epsilon \sim 10^{-5}mc^2$ . Therefore, in this unscreened region, the valence electrons in a neutral atom behave in the same way as a weakly bound electron in a Coulomb potential. That is, in this region, the wave functions of electrons in a neutral atom  $\varphi$  are proportional to the electron wave functions  $\varphi_H$  of hydrogen-like ions with high principal quantum number. Therefore, to good accuracy,

$$\langle \varphi | V_{SE}(\mathbf{r}, \mathbf{r}', \epsilon) | \varphi \rangle = \langle \varphi_H | V_{SE}(\mathbf{r}, \mathbf{r}', \epsilon) | \varphi_H \rangle \frac{\rho(r_n)}{\rho_H(r_n)}, \quad (1)$$

where  $\rho(r_n) = \varphi^\dagger(r_n)\varphi(r_n)$  is the density of the electron wave function at the nucleus and the subscript ‘‘H’’ refers

to the case for hydrogen-like ions. Since the Uehling potential is localized in the nuclear vicinity, the expression above may also be written as

$$\delta\epsilon_{SE} = \delta\epsilon_{SE,H} \frac{\delta\epsilon_{Ueh}}{\delta\epsilon_{Ueh,H}}, \quad (2)$$

where  $\delta\epsilon_{SE} = \langle \varphi | V_{SE}(\mathbf{r}, \mathbf{r}', \epsilon) | \varphi \rangle$  and  $\delta\epsilon_{Ueh} = \langle \varphi | V_{Ueh} | \varphi \rangle$  are the self-energy and Uehling corrections to the binding energy. This relation was used in Ref. [31] to estimate self-energy valence  $s$ -wave shifts to binding energies and later confirmed by rigorous self-energy calculations in Ref. [14]. In a similar manner, based around Welton’s idea of the fluctuating position of the electron, where the dominant part of the self-energy shift for the  $s$ -waves is proportional to  $\nabla^2 V(\mathbf{r})$  and  $V(\mathbf{r})$  is the potential seen by the electron [25], the self-energy shift may be approximated by the ratio  $\delta\epsilon_{SE} = \delta\epsilon_{SE,H} \langle \varphi | \nabla^2 V(\mathbf{r}) | \varphi \rangle / \langle \varphi_H | \nabla^2 V(\mathbf{r}) | \varphi_H \rangle$ , Ref. [24]. See also Ref. [23] for a recent implementation of this approach and for other references. For states  $l > 0$ , the ratio  $\delta\epsilon_{SE} = \delta\epsilon_{SE,H} \langle \varphi | \beta \boldsymbol{\alpha} \cdot \nabla V(\mathbf{r}) | \varphi \rangle / \langle \varphi_H | \beta \boldsymbol{\alpha} \cdot \nabla V(\mathbf{r}) | \varphi_H \rangle$  has been proposed [32], where  $\beta$  and  $\boldsymbol{\alpha}$  are Dirac matrices.

Using the ratio methods above, one may yield reasonable estimates for the self-energy corrections for valence  $s$  orbitals of atoms and ions. However, for estimating shifts for orbitals with  $l > 0$ , this procedure may prove to be cumbersome or inadequate, since core relaxation corrections determine the size and the sign of the effect [8, 30, 33].

The goal, then, is to extract from Eq. (1) a local potential that, when averaged over an orbital’s wave function, gives the one-loop self-energy correction to the energy of the orbital. This potential may then be added to many-body atomic structure codes in a simple manner. One may expect, from examination of Eq. (1), that as long as self-energy shifts for hydrogen-like ions are reproduced with high accuracy by such a potential, the accuracy for self-energy shifts for neutral atoms should also be high.

It is worth noting that the local potential that was isolated from the non-local model operator considered in the work of Shabaev *et al.* [27] was fitted to the (tightly-bound)  $1s$  state of hydrogen-like ions and then applied to the (loosely-bound) valence  $s$  levels in neutral atoms. This is likely the reason for the deviations on the order of 10% from the results of exact QED for calculations in frozen atomic potentials. Indeed, from Table VI in their work Ref. [27], it is seen that their local potential produces shifts for the  $5s$  level in hydrogen-like ions that deviate from the exact self-energy shifts by about 30% for the heavier ions considered in that table,  $40 \leq Z \leq 92$ .

In the FGRP approach, the self-energy part of the radiative potential contains a magnetic formfactor term and an electric formfactor term, divided into high- and low-frequency components,

$$V_{SE}(\mathbf{r}) = V_{mag}(\mathbf{r}) + V_{high}(r) + V_{low}(r). \quad (3)$$

TABLE I. Self-energy corrections to the binding energies for  $s$ ,  $p_{1/2}$ ,  $p_{3/2}$ ,  $d_{3/2}$ , and  $d_{5/2}$  states for hydrogen-like ions. Point-nucleus results of the radiative potential (FGRP) are compared with exact self-energy point-nucleus calculations [27, 34, 35]. The shifts are expressed as values of the function  $F(Z\alpha)$ , Eq. (8).

Ion	Z	n	$F(Z\alpha)$									
			$ns$		$np_{1/2}$		$np_{3/2}$		$nd_{3/2}$		$nd_{5/2}$	
			FGRP	Exact <sup>a</sup>	FGRP	Exact <sup>a</sup>	FGRP	Exact <sup>a</sup>	FGRP	Exact <sup>a</sup>	FGRP	Exact <sup>a</sup>
Na	11	2	4.7878	4.6951	-0.0796	-0.1129	0.1656	0.1316				
		3	4.7832	4.7530	-0.0876	-0.0998	0.1568	0.1434	-0.0416	-0.0426	0.0419	0.0409
		4	4.7808	4.7753	-0.0892	-0.0940	0.1548	0.1487	-0.0401	-0.0406	0.0434	0.0429
		5	4.7792	4.7860	-0.0898	-0.0908	0.1540	0.1516	-0.0395	-0.0394	0.0440	0.0441
K	19	3	3.6825	3.6550	-0.0628	-0.0790	0.1740	0.1555	-0.0409	-0.0421	0.0427	0.0416
		4	3.6784	3.6754	-0.0643	-0.0721	0.1718	0.1612	-0.0393	-0.0400	0.0444	0.0438
		5	3.6753	3.6845	-0.0648	-0.0685	0.1709	0.1644	-0.0386	-0.0388	0.0451	0.0450
Rb	37	3	2.6315	2.6041	0.0033	-0.0165	0.2149	0.1910	-0.0389	-0.0401	0.0455	0.0445
		4	2.6220	2.6186	0.0024	-0.0066	0.2122	0.1982	-0.0367	-0.0376	0.0478	0.0472
		5	2.6144	2.6227	0.0022	-0.0015	0.2110	0.2018	-0.0359	-0.0362	0.0487	0.0486
Cs	55	4	2.2172	2.2045	0.0894	0.0805	0.2556	0.2431	-0.0325	-0.0334	0.0530	0.0523
		5	2.2027	2.2012	0.0891	0.0867	0.2540	0.2475	-0.0313	-0.0316	0.0542	0.0542
		6	2.1915		0.0889		0.2531		-0.0307		0.0549	
Fr	87	5	2.0939	2.0965	0.3429	0.3465	0.3438	0.3469	-0.0144	-0.0135	0.0700	0.0687
		6	2.0637		0.3388		0.3419		-0.0131		0.0712	
		7	2.0404		0.3354		0.3404		-0.0124		0.0719	
E119	119	5	3.0499	3.0642	1.1687	1.257	0.4750	0.4686	0.0283	0.0311	0.0970	0.0880
		6	2.9407		1.1299		0.4714		0.0309		0.0994	
		7	2.8596		1.1006		0.4682		0.0323		0.1006	
		8	2.7975		1.0778		0.4654		0.0331		0.1012	

<sup>a</sup> Values found by interpolation of the exact calculations of Shabaev *et al.*, consistent with those of Mohr and Kim [34] and Le Bigot *et al.* [35].

For the point-nucleus case  $V_{\text{nuc}}^{\text{point}} = Z/r$ , the potentials have the form [8]

$$V_{\text{mag}}^{\text{point}}(\mathbf{r}) = \frac{i\alpha^2}{4\pi} \boldsymbol{\gamma} \cdot \nabla \left[ \left( \frac{Z}{r} \right) \left( \int_1^\infty dt \frac{1}{t^2 \sqrt{t^2 - 1}} e^{-2tr/\alpha} - 1 \right) \right], \quad (4)$$

$$V_{\text{high}}^{\text{point}}(r) = -A_l(Z, r) \left( \frac{\alpha}{\pi} \right) \left( \frac{Z}{r} \right) \int_1^\infty dt \frac{1}{\sqrt{t^2 - 1}} \left[ \left( 1 - \frac{1}{2t^2} \right) [\ln(t^2 - 1) + 4 \ln(1/Z\alpha + 1/2)] - \frac{3}{2} + \frac{1}{t^2} \right] e^{-2tr/\alpha}, \quad (5)$$

$$V_{\text{low}}^{\text{point}}(r) = -B_l(Z) Z^4 \alpha^3 e^{-Zr}, \quad (6)$$

where  $\boldsymbol{\gamma} = \beta\boldsymbol{\alpha}$  is a Dirac matrix. The coefficients  $A_l(Z, r) = A_l(Z) r / (r + 0.07Z^2\alpha^3)$  and  $B_l(Z)$  are fitting factors, and in Ref. [8] they were found by fitting to the  $5s$ ,  $5p_{1/2}$ , and  $5p_{3/2}$  self-energy shifts for hydrogen-like ions [34]. In that work, a single local potential was formed with no dependence on the orbital angular momentum quantum number  $l$ . In the current work, we

introduce an  $l$ -dependence to the potential in order to control the shifts to  $d$  levels and to improve the potential's accuracy for use in many-body calculations.

We keep the same fitting factors as those in Ref. [8] for the  $s$  and  $p$  levels, and for  $d$  levels we introduce different factors, optimized to fit  $5d_{3/2}$  and  $5d_{5/2}$  self-energy shifts in hydrogen-like ions [27, 34, 35],

$$\begin{aligned}
A_l(Z) &= \begin{cases} 1.071 - 1.976x^2 - 2.128x^3 + 0.169x^4, & l = 0, 1 \\ 0, & l = 2, \end{cases} \\
B_l(Z) &= \begin{cases} 0.074 + 0.35Z\alpha, & l = 0, 1 \\ 0.056 + 0.050Z\alpha + 0.195Z^2\alpha^2, & l = 2, \end{cases}
\end{aligned} \tag{7}$$

where  $x = (Z - 80)\alpha$ . For  $l > 2$ , we set  $A_l(Z)$  and  $B_l(Z)$  to zero. The magnetic term is exact to first-order in  $Z\alpha$ , and no fitting factors are introduced for it.

In Table I we present the self-energy shifts for hydrogen-like ions obtained using the point-nucleus radiative potential, Eqs. (4), (5), (6). The shifts  $\delta\epsilon_{\text{SE}}$  may be expressed as values of the function  $F(Z\alpha)$  according to the relation [34]

$$\delta\epsilon_{\text{SE}} = \frac{\alpha}{\pi} \frac{(Z\alpha)^4}{n^3} F(Z\alpha) mc^2. \tag{8}$$

Our results for  $F(Z\alpha)$  are tabulated alongside the results of exact self-energy calculations [27, 34, 35]. The agreement for  $n = 5$  is particularly good, since the parameters of the radiative potential were found by fitting to these levels. For  $5s$ , the deviations across all  $Z$  are on the order of 0.1%. For other  $s$  states presented in the table, the largest deviation is for Na  $2s$ , where it is 2%. For the  $5p$  states, the deviation is typically on the level of 1%. However, around the nuclear charge for Rb, the self-energy shifts for  $p_{1/2}$  transition from negative to positive, and

for Rb our radiative potential yields the wrong sign for the shift, although the size of the shift is very small. It is seen from Table I that the shifts for the  $p$  waves with lower principal quantum number  $n$  deviate further from the exact calculations, on the order of 10%. For the  $d$  levels considered, the radiative potential is typically accurate to a few percent. In Table I we have presented shifts for those states that we consider to be of relevance in the study of neutral atoms. In particular, valence level shifts for  $s$ ,  $p$ , and  $d$  waves, and the shifts corresponding to the uppermost core  $s$ ,  $p$ , and  $d$  waves, which affect the valence shifts through relaxation effects.

To obtain the finite-nucleus expressions for use in atomic codes, the point-nucleus expressions for the radiative potential are folded with the nuclear density  $\rho_{\text{nuc}}$ ,

$$V_{\text{SE}}^{\text{fin}}(\mathbf{r}) = \frac{1}{Z} \int d^3r' V_{\text{SE}}^{\text{point}}(|\mathbf{r} - \mathbf{r}'|) \rho_{\text{nuc}}(\mathbf{r}'), \tag{9}$$

where the nuclear density is normalized as  $\int \rho_{\text{nuc}}(\mathbf{r}) d^3r = Z$ . We find the following finite-nuclear-size expressions for the case of spherical symmetry of the nuclear density  $\rho_{\text{nuc}}(\mathbf{r}) = \rho_{\text{nuc}}(r)$ ,

$$V_{\text{mag}}^{\text{fin}}(\mathbf{r}) = \frac{i\alpha^3}{4} \boldsymbol{\gamma} \cdot \boldsymbol{\nabla} \frac{1}{r} \int_0^\infty dr' \int_1^\infty dt \frac{1}{t^3 \sqrt{t^2 - 1}} \rho_{\text{nuc}}(r') r' \left[ (e^{-2t|r-r'|/\alpha} - e^{-2t(r+r')/\alpha}) - \frac{2t}{\alpha} (r + r' - |r - r'|) \right] \tag{10}$$

$$\begin{aligned}
V_{\text{high}}^{\text{fin}}(r) &= A_l(Z) \frac{\alpha}{r} \int_0^\infty dr' r' \rho_{\text{nuc}}(r') \int_1^\infty dt \frac{1}{\sqrt{t^2 - 1}} \left[ \left(1 - \frac{1}{2t^2}\right) [\ln(t^2 - 1) + 4 \ln(1/Z\alpha + 1/2)] - \frac{3}{2} + \frac{1}{t^2} \right] \times \\
&\quad \left\{ \frac{\alpha}{t} \left( e^{-2t(r+r')/\alpha} - e^{-2t|r-r'|/\alpha} \right) + 2r_A e^{2r_A t/\alpha} \left( E_1[|r - r'| + r_A] 2t/\alpha - E_1[(r + r' + r_A) 2t/\alpha] \right) \right\}
\end{aligned} \tag{11}$$

$$V_{\text{low}}^{\text{fin}}(r) = -B_l(Z) \frac{2\pi Z\alpha^3}{r} \int_0^\infty dr' r' \rho_{\text{nuc}}(r') \left[ (Z|r - r'| + 1) e^{-Z|r-r'|} - (Z(r + r') + 1) e^{-Z(r+r')} \right] \tag{12}$$

where  $E_1(x) = \int_x^\infty ds (e^{-s}/s)$  is the exponential integral

and  $r_A = 0.07Z^2\alpha^3$ . We reduce these integrals further by considering the nucleus to be modelled as a homogeneously charged sphere (step-function density),

$$V_{\text{mag}}^{\text{step}}(\mathbf{r}) = \begin{cases} \frac{3Zi}{\pi} \boldsymbol{\gamma} \cdot \mathbf{n} \int_1^\infty dt \frac{1}{\varkappa^3 \sqrt{t^2-1}} \left( \frac{\alpha}{2tr} \right)^2 \left\{ e^{-\varkappa} (1 + \varkappa) [\sinh(\frac{2tr}{\alpha}) - \frac{2tr}{\alpha} \cosh(\frac{2tr}{\alpha})] + \frac{1}{3} \left( \frac{2tr}{\alpha} \right)^3 \right\}, & r \leq r_n \\ \frac{3Zi}{\pi} \boldsymbol{\gamma} \cdot \mathbf{n} \int_1^\infty dt \frac{1}{\varkappa^3 \sqrt{t^2-1}} \left( \frac{\alpha}{2tr} \right)^2 \left\{ e^{-2tr/\alpha} (1 + 2tr/\alpha) [\sinh \varkappa - \varkappa \cosh \varkappa] + \frac{1}{3} \varkappa^3 \right\}, & r > r_n \end{cases}, \quad (13)$$

$$V_{\text{high}}^{\text{step}}(r) = \begin{cases} -\frac{3}{2} A_l(Z) \frac{\alpha}{\pi} \frac{Z}{r} \int_1^\infty dt I_1(t, Z) \left\{ e^{-2tr/\alpha} \left( \frac{2}{\varkappa^3} \right) [\varkappa \cosh \varkappa - \sinh \varkappa] - \frac{r_A}{r_n^3} I_2(t, r, Z) \right\}, & r \leq r_n \\ -\frac{3}{2} A_l(Z) \frac{\alpha}{\pi} \frac{Z}{r} \int_1^\infty dt I_1(t, Z) \left\{ \frac{2}{\varkappa^3} \left[ \frac{r}{r_n} \varkappa - e^{-\varkappa} (1 + \varkappa) \sinh(2tr/\alpha) \right] - \frac{r_A}{r_n^3} I_2(t, r, Z) \right\}, & r > r_n \end{cases}, \quad (14)$$

$$V_{\text{low}}^{\text{step}}(r) = -\frac{3}{2} B_l(Z) \frac{Z^2 \alpha^3}{r_n^3} \int_0^{r_n} dr' r' \left[ (Z|r-r'|+1) e^{-Z|r-r'|} - (Z(r+r')+1) e^{-Z(r+r')} \right], \quad (15)$$

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where  $r_n$  is the nuclear radius,  $\varkappa = 2tr_n/\alpha$ , and

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$$I_1(t, Z) = \frac{1}{\sqrt{t^2-1}} \left[ \left( 1 - \frac{1}{2t^2} \right) \left[ \ln(t^2-1) + 4 \ln \left( \frac{1}{Z\alpha} + \frac{1}{2} \right) \right] - \frac{3}{2} + \frac{1}{t^2} \right] \quad (16)$$

$$I_2(t, r, Z) = \int_0^{r_n} dr' r' e^{2r_A t/\alpha} \left( E_1[|r-r'|+r_A] 2t/\alpha - E_1[(r+r'+r_A) 2t/\alpha] \right). \quad (17)$$

This is the form of the radiative potential we use in subsequent calculations,  $V_{\text{SE}}(\mathbf{r}) = V_{\text{SE}}^{\text{step}}(\mathbf{r})$ . The nuclear radii for the step-function density are found from the root-mean-square radii  $r_{\text{rms}}$  tabulated in Ref. [36],  $r_n = \sqrt{5/3} r_{\text{rms}}$ . For E119, we take  $r_{\text{rms}} = 6.5$  fm, consistent with Hartree-Fock-BCS theory [37]. We have carried out numerical integration for the improper integrals (integration over the variable  $t$ ) using the GNU Scientific Library routine QAGI [38].

We have checked the validity of the step-density approximation by performing calculations for first-order self-energy shifts using a two-parameter Fermi distribution for the nuclear density in Eqs. (10), (11), (12). We took the 90% to 10% fall-off to be 2.3 fm for all atoms, and the half-density radius was found from this and from  $r_{\text{rms}}$  (above). We have found agreement to all digits presented, and therefore suggest the use of the simpler step-function form for the integrals. Energy shifts arising from the long-ranged  $V_{\text{low}}(r)$  are insensitive to nuclear size, and the point-nucleus expression Eq. (6) may be used in place of Eq. (15). For the magnetic formfactor term  $V_{\text{mag}}(\mathbf{r})$ , differences between the use of the point-nucleus and finite-nucleus expressions appear in the energy shifts only for high  $Z$ .

### III. FIRST-ORDER SHIFTS AND COMPARISON WITH EXACT QED

In this section we calculate the first-order valence self-energy shifts in different atomic potentials. Comparison of our results using the radiative potential with results of exact self-energy calculations performed in the same atomic potentials gives us a reliable indication of the accuracy of our approach.

The first-order shifts to the binding energies of the valence electron are given by

$$\delta \epsilon_i^{(1)} = -\langle \varphi_i | V_{\text{SE}} | \varphi_i \rangle. \quad (18)$$

The orbitals are found from the solution of the relativistic equations

$$(c\boldsymbol{\alpha} \cdot \mathbf{p} + (\beta - 1)c^2 - V_{\text{nuc}} - V_{\text{el}}) \varphi_i = \epsilon_i \varphi_i, \quad (19)$$

where  $\boldsymbol{\alpha}$  and  $\beta$  are Dirac matrices,  $\mathbf{p}$  is the momentum operator, and  $V_{\text{nuc}}$  and  $V_{\text{el}}$  are the nuclear and electronic potentials. In our atomic structure calculations, we use a nuclear potential corresponding to a two-parameter Fermi distribution for the nuclear density; the parameters are given in the final paragraph of the previous section. We consider three different electronic potentials in this paper: core-Hartree  $V_{\text{CH}}$ , Kohn-Sham  $V_{\text{KS}}$ , and relativistic Hartree-Fock  $V_{\text{HF}}$ . The first two are considered for comparison with exact self-energy calculations performed in the same atomic potentials (from Ref. [15]) while the Hartree-Fock potential is the starting point of our calculations in many-body perturbation theory. For more details about the core-Hartree and Kohn-Sham potentials, we refer the reader to Ref. [15]; for explicit expressions for the relativistic Hartree-Fock potential, see Ref. [39].

We use the following form for the relativistic orbitals

$$\varphi = \frac{1}{r} \begin{pmatrix} f(r) \Omega_{\kappa m} \\ i\alpha g(r) \tilde{\Omega}_{\kappa m} \end{pmatrix}, \quad (20)$$

where  $f$  and  $g$  are upper and lower radial components, the spherical spinor  $\Omega_{\kappa m} = -(\boldsymbol{\sigma} \cdot \mathbf{n}) \Omega_{\kappa m} = \Omega_{-\kappa m}$ , and the angular momentum quantum number  $\kappa = \mp(j+1/2)$  for  $j = l \pm 1/2$ ;  $l$  is the orbital angular momentum and

$j$  the total angular momentum, with  $m$  its projection on the  $z$  axis.

The first-order valence shifts arising from the electric parts of the radiative potential are

$$\delta\epsilon_{\text{high}}^{(1)} = - \int_0^\infty dr V_{\text{high}}(f^2 + \alpha^2 g^2) \quad (21)$$

$$\delta\epsilon_{\text{low}}^{(1)} = - \int_0^\infty dr V_{\text{low}}(f^2 + \alpha^2 g^2) \quad (22)$$

and the first-order shift from the magnetic formfactor is

$$\delta\epsilon_{\text{mag}}^{(1)} = -2 \int_0^\infty dr f g H(r), \quad (23)$$

where we have expressed the magnetic potential in terms of a function  $H(r)$  which we have defined such that

$$V_{\text{mag}}(\mathbf{r}) = i\boldsymbol{\gamma} \cdot \mathbf{n} H(r)/\alpha. \quad (24)$$

### A. Core-Hartree and Kohn-Sham

In Table II we present our core-Hartree results for Cs  $6s$ , with contributions from the magnetic and the electric components given separately. We present results corresponding to the use of different nuclear approximations for the radiative potential: point-like, step-function density, and two-parameter Fermi distribution. For Cs and all other atoms considered in this work, we have found no difference, to all digits presented, between the use of the step-function density (Eqs. (13), (14), (15)) and that of the Fermi distribution (Eqs. (10), (11), (12)) with the same root-mean-square radius.

In calculations of exact QED in frozen atomic potentials, an effective charge is used [15]. This effective charge includes a screening of the nuclear charge by the electrons. For comparison with exact QED, we should therefore include this screening by the electrons. We do so in a simple manner by replacing in Eqs. (10), (11), (12) the nuclear density  $\rho_{\text{nuc}}$  with the density of the electron core  $\rho_{\text{el}}(r)$  normalized such that  $\int \rho_{\text{el}}(r) d^3r = -N_{\text{core}}$ , where  $N_{\text{core}} = Z - 1$  is the number of electrons in the core. This screening term for Cs  $6s$  in the core-Hartree approximation is given in the second last row of Table II.

In Table III we present our self-energy results for the valence  $s$  level shifts for Na through to Fr in the core-Hartree and the Kohn-Sham approximations. Our results include electronic screening, taken into account in the core-Hartree approximation in the manner described above. Our results are presented alongside the exact self-energy shifts [15] found in the same atomic potentials. Results of the model operator approach of Shabaev *et al.* [27] are shown also. It is remarkable how well the radiative potential approximates the exact self-energy in neutral atoms, at the level of about 1%. E.g., for Na  $3s$  in the Kohn-Sham approximation, we obtain the value  $F = 0.185$ , while the exact value is  $F = 0.181$ . The agreement is even better for the heavier atoms. The size

of the deviation is only about twice the deviation seen between the results of the model operator approach and the exact formalism.

### B. Hartree-Fock

The relativistic Hartree-Fock approximation is the starting point for our treatment of many-body effects, as in this approximation many-body perturbation theory in the residual Coulomb interaction is simplified; see Section V. Therefore, we begin by considering the first-order valence self-energy corrections in the relativistic Hartree-Fock approximation.

Note that in this and subsequent sections, we do not include in our calculations the electronic density (or “screening”) correction considered in Section III A.

Our first-order results for the lowest  $s$ ,  $p$ , and  $d$  valence levels are presented in the fifth column of Table VI. The  $s$ -level shifts range from about  $10^{-5}$  a.u. for Na to nearly  $10^{-3}$  a.u. for E119. Of course, the  $p$  and  $d$  shifts are progressively smaller due to the short-range nature of the self-energy interaction. While the shifts from the electric part of the potential lead to a reduction in the binding energies for all states, the magnetic part of the potential leads to shifts in the energies that are of opposite sign for those levels with positive angular quantum number  $\kappa$ , i.e., for  $p_{1/2}$  and  $d_{3/2}$  waves. In some cases this leads to a delicate cancellation between the shifts arising from the magnetic formfactor and from the low-frequency part of the electric formfactor. For example, for Cs  $6p_{1/2}$ , the magnetic part of the potential contributes  $-0.2481 \times 10^{-5}$  a.u. and the low-frequency electric part of the potential contributes  $+0.2491 \times 10^{-5}$  a.u. The low-frequency part of the potential contains factors found by fitting to the hydrogen-like  $5p_{1/2}$  shift, and for this case there is also a degree of cancellation between the terms (leaving a few percent of the size of one term). Since the magnetic and electric terms are treated so differently in the atomic structure calculations, a slight alteration in the orbitals can produce a significant change in the shift of the level. This limits the accuracy with which we can calculate the Cs  $6p_{1/2}$  shift. However, the size of this shift is small.

In some cases, the magnetic shift dominates and the overall shift, like the vacuum polarization contribution, is negative and leads to increased binding.

## IV. CORE RELAXATION

In this and the following section we will consider how the account of many-body effects, in particular core relaxation and correlations between the valence electron and the core, influences the self-energy shifts in neutral atoms.

Core relaxation effects are found by adding the radiative potential to the potential felt by the core elec-

TABLE II. Breakdown of contributions to the first-order valence self-energy shift, using the FGRP method, to the Cs 6s binding energy in the core-Hartree approximation. Results for different nuclear approximations are given. Units:  $10^{-5}$  a.u. The final, screened finite-nucleus result  $8.608 \times 10^{-5}$  a.u. corresponds to the value  $F(Z\alpha) = 0.01643$ , presented in Table III.

Density approximation	$\delta\epsilon_{\text{mag}}^{(1)}$	$\delta\epsilon_{\text{high}}^{(1)}$	$\delta\epsilon_{\text{low}}^{(1)}$	$\delta\epsilon^{(1)}$
Point-nucleus	1.391	6.583	0.762	8.736
Step-function	1.391	6.577	0.762	8.730
Fermi distribution	1.391	6.577	0.762	8.730
Electron core	-0.013	-0.043	-0.065	-0.121
Finite nucleus, screened	1.378	6.534	0.697	8.608

trons, in this case the Hartree-Fock potential of the core,  $V_{\text{HF}} + V_{\text{SE}}$ , and solving the relativistic equations (19) for the core electrons self-consistently. This leads to a new Hartree-Fock potential  $V_{\text{HF}}^{\text{SE}}$ . The correction to the zeroth-order Hartree-Fock potential  $V_{\text{HF}}$  is  $\delta V_{\text{HF}}^{\text{SE}} = V_{\text{HF}}^{\text{SE}} - V_{\text{HF}}$ ; this may be referred to as the relaxation correction to the potential.

The self-energy correction to the binding energy of the valence electron may then be expressed as

$$\delta\epsilon_i = -\langle\varphi_i|V_{\text{SE}} + \delta V_{\text{HF}}^{\text{SE}}|\varphi_i\rangle = \delta\epsilon_i^{(1)} + \delta\epsilon_i^{\text{relax}}. \quad (25)$$

In actual calculations, however, we find the energies  $\epsilon'_i$  from the solution of the equation

$$(c\boldsymbol{\alpha} \cdot \mathbf{p} + (\beta - 1)c^2 - V_{\text{nuc}} - V_{\text{SE}} - V_{\text{HF}}^{\text{SE}})\varphi'_i = \epsilon'_i\varphi'_i. \quad (26)$$

The correction is given by

$$\delta\epsilon_i = \epsilon'_i - \epsilon_i. \quad (27)$$

Note that energies from the solution of Eqs. (26), (27) include higher orders of the self-energy not contained in Eq. (25).

It is a simple matter to include the electric parts of the radiative potential into the atomic structure codes. They may be added to the Hartree-Fock or the nuclear

potential, as is done for Uehling [30, 33]. Inclusion of the (off-diagonal) magnetic part of the radiative potential is more involved, and the Dirac equations must be modified accordingly,

$$\begin{aligned} \frac{df}{dr} &= [-\kappa/r + H(r)]f + [2 + \alpha^2(\epsilon + V)]g \\ \frac{dg}{dr} &= -(\epsilon + V)f + [\kappa/r - H(r)]g, \end{aligned} \quad (28)$$

where the magnetic term appears through the introduction of  $H(r)$ , defined by Eq. (24). Here, the atomic potential includes the electric part of the radiative potential,  $V = V_{\text{nuc}} + V_{\text{el}} + V_{\text{high}} + V_{\text{low}}$ .

In the sixth column of Table VI, our self-energy results with core relaxation included are presented. The corrections for  $s$  levels enter at around 5%. While the relaxation effect increases the size of the  $s$ -wave self-energy shift for the lighter atoms Na to Cs, interestingly (unlike what we observed for the vacuum polarization [30]) it decreases the size of the shift for Fr and E119.

In Table VI we present also the  $s$ -wave shifts calculated by Thierfelder and Schwerdtfeger [22]. They performed relativistic Hartree-Fock calculations with the radiative corrections treated perturbatively; they used a modified version of the radiative potential [8]. There is good agreement between their results and our core-relaxed results.

For orbitals with  $l > 0$ , account of the relaxation effect is absolutely crucial for obtaining the correct sign and size of the shift, as was seen for the vacuum polarization [30, 33]. While the self-energy interaction is short-ranged, the relaxation potential  $\delta V_{\text{HF}}^{\text{SE}}$  is long-ranged, making corrections to  $p$  and  $d$  waves significant. The trend in the sign and size of the shifts is less straightforward than what we observed for the very short-ranged Uehling potential [30] due to the more complex form of the self-energy. It is not always clear from the start whether the shift will be positive or negative. The relaxation potential often produces a shift of the opposite sign as the first-order shift, and this may lead to a suppression of the first-order shift or a change in the sign and magnitude of the shift. Moreover, as we mentioned in the previous section, for  $p_{1/2}$  and  $d_{3/2}$  levels the different sign of the magnetic shift may produce a high level of cancellation between terms. The change in the core potential may disturb this cancellation, making the shift relatively large.

TABLE III. Finite-nucleus self-energy results  $\delta\epsilon^{(1)}$  for neutral atoms in core-Hartree and Kohn-Sham potentials are presented, expressed as the function  $F(Z\alpha)$ . The results of this work (FGRP) are given alongside those of exact QED and the model operator.

Atom	Z	State	$F(Z\alpha)$					
			core-Hartree		Kohn-Sham			
			FGRP	Exact <sup>a</sup>	FGRP	Exact <sup>a</sup>	Model <sup>b</sup>	
Na	11	3s	0.196	0.191	0.185	0.181	0.183	
K	19	4s	0.088	0.086	0.084	0.083	0.083	
Rb	37	5s	0.0291	0.0286	0.0287	0.0283	0.0284	
Cs	55	6s	0.0164	0.0162	0.0164	0.0162	0.0163	
Fr	87	7s	0.0096	0.0096	0.0098	0.0098	0.0099	

<sup>a</sup> Sapirstein and Cheng, Ref. [15].

<sup>b</sup> Shabaev *et al.*, Ref. [27].

TABLE IV. Contributions to the self-energy relaxation shifts  $\delta\epsilon^{\text{relax}}$  for Cs found using the FGRP method. First-order valence shifts,  $\delta\epsilon^{(1)}$ , are shown in column two for comparison. Contributions to relaxation shifts arising from self-energy corrections to individual core  $s$  orbitals are given in columns 3 to 7, contributions from self-energy corrections to core  $s$ , core  $p_{1/2}$ , core  $p_{3/2}$ , core  $d_{3/2}$ , and core  $d_{5/2}$  are presented in columns 8 to 12. The total relaxation shifts,  $\delta\epsilon^{\text{relax}}$ , are given in the final column. Units: a.u.

State	$\delta\epsilon^{(1)}$	Contributions to the relaxation shift, $\delta\epsilon^{\text{relax}} \times 10^5$										$\delta\epsilon^{\text{relax}}$
	$\times 10^5$	1s	2s	3s	4s	5s	core $s$	core $p_{1/2}$	core $p_{3/2}$	core $d_{3/2}$	core $d_{5/2}$	$\times 10^5$
6s <sub>1/2</sub>	8.128	0.025	0.106	0.125	0.189	0.472	0.917	-0.064	-0.506	0.007	-0.014	0.341
6p <sub>1/2</sub>	0.108	-0.030	-0.024	-0.021	-0.037	-0.218	-0.329	0.011	-0.170	0.005	-0.007	-0.491
6p <sub>3/2</sub>	0.318	-0.018	-0.020	-0.015	-0.033	-0.242	-0.328	-0.024	-0.053	0.004	-0.009	-0.410
5d <sub>3/2</sub>	-0.061	0.078	0.017	-0.036	-0.062	-0.732	-0.735	-0.086	-0.324	-0.011	0.005	-1.151
5d <sub>5/2</sub>	0.072	0.073	0.019	-0.035	-0.064	-0.693	-0.700	-0.038	-0.461	-0.003	0.016	-1.186

The trend for the heavier elements is that the shifts for valence  $d$  waves is larger than the shifts for  $p$  waves, and that the size of the  $d$ -wave shifts can be less than an order of magnitude smaller than the  $s$ -wave shifts. For Cs, in the relaxed Hartree-Fock approximation, the  $5d$  shifts are only 7 to 8 times smaller than the  $6s$  shift and of opposite sign.

Contributions to the relaxation shifts for Cs arising from the radiative corrections to individual  $s$  states of the core and from radiative corrections to core  $p_{1/2}$ ,  $p_{3/2}$ ,  $d_{3/2}$  and  $d_{5/2}$  states are given in Table IV. It is seen that for all valence states, the relaxation shift comes mostly from the radiative corrections to core  $s$  states, with the uppermost core state giving the largest part of this shift. The contributions from core  $p$  states are also significant, with those from  $d$  states small but non-negligible.

The relaxed self-energy shifts show a similar pattern overall with the relaxed vacuum polarization (Uehling) shifts [30]. The Uehling potential is extremely short-ranged, making the relative size of the relaxation correction for  $d$  waves orders of magnitude larger than what we see for the self-energy. The relative size of the relaxed  $d$ -wave shift to relaxed  $s$ -wave shift, however, is roughly the same for the vacuum polarization and self-energy cases. We can understand this by noting that most of the relaxation shift for  $d$  waves (for the vacuum polarization and the self-energy) arises from the radiative corrections to the uppermost  $s$  wave of the core.

Indeed, much of the effect for the  $s$  and  $d$  shifts can be determined by limiting the consideration to the radiative shifts to  $s$  waves only. The valence  $s$ -level shift largely arises from the first-order valence shift; the valence  $d$ -level shift arises largely from the radiative  $s$ -wave shift to the core. The largest part of the self-energy shift to the  $s$  waves comes from the high-frequency part of the electric formfactor term, and this term is rather similar in form to the Uehling potential. We understand this to be the reason for the comparable size of the ratio of the  $d$ - to  $s$ -wave shifts for both vacuum polarization and self-energy.

For the  $p$  waves, the first-order valence shift and the shift arising from the relaxation of the core are often close

in magnitude and of opposite sign. Here, the radiative corrections to both  $s$  and  $p$  waves must be considered.

## V. CORRELATION CORRECTIONS

Use of the Hartree-Fock method as the starting approximation simplifies the perturbation theory in the residual Coulomb interaction,  $1/|\mathbf{r}_i - \mathbf{r}_j| + V_{\text{HF}}$ , where  $V_{\text{HF}}$  is the Hartree-Fock potential. The first non-vanishing correction for the interaction of the valence electron with the core appears in the second order in the Coulomb interaction. Diagrams of these second-order correlation corrections to the valence energies may be found in, e.g., Refs. [9, 40].

A non-local, energy-dependent potential  $\Sigma^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \epsilon_i)$  may be formed, defined such that its averaged value over the valence electron orbitals corresponds to the correlation correction to the orbital energies,  $\delta\epsilon_i^{(2)} = \langle \varphi_i | \Sigma^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \epsilon_i) | \varphi_i \rangle$ . This potential is termed the “correlation potential”. This potential may be added to the relativistic Hartree-Fock equations for the valence electron, yielding so-called Brueckner orbitals  $\varphi_{\text{Br},i}$  and energies  $\epsilon_{\text{Br},i}$ . This method takes into account the higher orders in  $\Sigma$  in the Brueckner orbitals and energies. The method of utilizing a potential to include correlations is called the *correlation potential method*.

Perturbation theory in the residual Coulomb interaction does not converge rapidly; in some cases, the third-order corrections are as large as the second [41]. Therefore, it is important to take into account dominating classes of diagrams to all orders in the Coulomb interaction. A method for taking into account the higher orders of perturbation theory in the residual Coulomb interaction was developed by Dzuba, Flambaum, and Sushkov [42]. In their method, the Coulomb lines in the second-order correlation potential are modified to include an infinite series of core polarization loops and an infinite series of hole-particle interactions in those loops through the use of the Feynman diagram technique. In this case, the correlation correction to the energy may be expressed as  $\delta\epsilon_i^{(\infty)} = \langle \varphi_i | \Sigma^{(\infty)}(\mathbf{r}_1, \mathbf{r}_2, \epsilon_i) | \varphi_i \rangle$ . Again, this potential



TABLE V. First-order valence self-energy corrections to the binding energies for Cs in the FGRP approach,  $\delta\epsilon_{\text{Br}}^{(1)} = -\langle\varphi_{\text{Br}}|V_{\text{SE}}|\varphi_{\text{Br}}\rangle$ , where  $\varphi_{\text{Br}}$  is a solution of the Brueckner equation  $(h_{\text{HF}} + f_{\kappa}\Sigma_{\kappa})\varphi_{\text{Br}} = \epsilon\varphi_{\text{Br}}$  and the correlation potential  $\Sigma$  is the second-order  $\Sigma^{(2)}$  or the all-orders  $\Sigma^{(\infty)}$ . With no fitting,  $f_{\kappa} = 1$  and  $\epsilon = \epsilon_{\text{Br}}$ , while with fitting  $\epsilon = \epsilon_{\text{exp}}$ . The numbers in square brackets [] denote powers of 10. Units: a.u.

State	$\epsilon_{\text{exp}}^{\text{a}}$	Second-order correlation potential $\Sigma^{(2)}$			All-orders correlation potential $\Sigma^{(\infty)}$		
		$\epsilon_{\text{Br}}$	$\delta\epsilon_{\text{Br}}^{(1)}$	$\delta\epsilon_{\text{Br,fit}}^{(1)}$	$\epsilon_{\text{Br}}$	$\delta\epsilon_{\text{Br}}^{(1)}$	$\delta\epsilon_{\text{Br,fit}}^{(1)}$
$6s_{1/2}$	-0.143098	-0.147671	1.225[-4]	1.134[-4]	-0.143262	1.120[-4]	1.118[-4]
$6p_{1/2}$	-0.092166	-0.093578	1.708[-6]	1.588[-6]	-0.092436	1.610[-6]	1.588[-6]
$6p_{3/2}$	-0.089642	-0.090849	4.875[-6]	4.563[-6]	-0.089848	4.626[-6]	4.574[-6]
$5d_{3/2}$	-0.077035	-0.080029	-1.521[-6]	-1.353[-6]	-0.078015	-1.414[-6]	-1.359[-6]
$5d_{5/2}$	-0.076590	-0.079296	1.744[-6]	1.561[-6]	-0.077501	1.629[-6]	1.568[-6]

<sup>a</sup> Data from NIST, Ref. [47].

may be added to the relativistic Hartree-Fock equations for the valence electron to yield all-order Brueckner orbitals and energies.

The all-orders correlation potential method is a simple and effective approach that leads to some of the most accurate calculations of properties of heavy atoms, most notably for alkali atoms. One example is the atomic parity violating amplitude in Cs [43–45].

Inclusion of the correlation potential modifies the valence orbitals at large distances,  $r \gtrsim a_B$ , pulling them towards the nucleus. This affects the form of the orbitals in the region where the self-energy interaction occurs through the normalization of the wave functions. See Ref. [30] for more details about the correlation effects at small distances, and an illustration of the modification to the orbitals.

The second-order correlation potential  $\Sigma^{(2)}$  is calculated using a B-spline basis set [46] obtained by diagonalizing the relativistic Hartree-Fock operator on a set of 40 splines of order  $k = 9$  within a cavity of radius 40 a.u. The exchange part of  $\Sigma^{(\infty)}$  is also considered in the second-order, with (multipolarity-dependent) factors used to screen the Coulomb interaction. For the direct part of  $\Sigma^{(\infty)}$ , the Feynman diagram technique is used for inclusion of the core polarization and hole-particle classes of diagrams; see Ref. [40] for further details about the method.

In the current work, we determine the effects on the self-energy shifts due to the use of the all-order Brueckner orbitals to take into account second and higher orders of perturbation theory in the residual Coulomb interaction. We calculate these shifts for Cs, though we simplify the method for inclusion of third and higher orders of perturbation theory for the shifts to Na through to E119 by using a trivial fitting procedure. Inclusion of the effects of higher orders of perturbation theory may be approximated simply by introducing factors before  $\Sigma^{(2)}$ , with a different factor for each partial wave  $\kappa$ . These factors are found by fitting the Brueckner energies to the experimental binding energies. The accuracy of calculations using the all-orders  $\Sigma^{(\infty)}$  may also be improved upon using this

method.

In our recent work on the vacuum polarization shifts [30], we demonstrated the effectiveness of this fitting procedure for Cs. In Table V of the current work, we illustrate this approach for the case of the self-energy shifts. Indeed, while the bare second-order Brueckner results for the self-energy shifts differ from the all-order results in the second digit, the fitted second-order results differ from the fitted all-order results in the third, or higher, digit. Therefore, we consider that the use of the fitted second-order correlation potential for determining the valence-core correlations is accurate to around 1% or better.

In the seventh column of Table VI, we present our “final” numbers for the self-energy shifts, taking into account both core relaxation and correlation corrections. The general trend in the effect of the Brueckner orbitals on the self-energy shifts is to increase the size of the shift, and the largest corrections occur for the  $d$ -wave shifts which are typically enhanced by a factor of two or more. This makes the relative size of the  $d$  wave to  $s$  wave shifts larger. For Cs, the self-energy shifts for the  $5d$  levels are only four to five times smaller than the  $6s$  shift.

## VI. DISCUSSION

We expect that our self-energy shifts for  $s$  and  $d$  levels are accurate to a few percent. The accuracy for at least some of the  $p$  level shifts is lower due to the competing first-order and relaxation contributions and the competition between the magnetic and electric parts of the shift.

The accuracy of the radiative potential is limited by how well it reproduces the self-energy shifts for hydrogen-like ions. In future applications, a  $\kappa$ -dependence could be introduced to further improve the accuracy. Indeed, a  $\kappa$ -dependent local potential is simple to implement and introduces no additional complexity in the many-body methods. All resulting wave functions remain orthogonal by virtue of the different angular dependence. This may be contrasted with the  $n$ -dependence introduced

TABLE VI. Self-energy corrections to binding energies in the FGRP approach. Experimental and zeroth-order relativistic Hartree-Fock binding energies are given in the third and fourth columns, respectively. First order valence corrections  $\delta\epsilon^{(1)} = -\langle\varphi|V_{SE}|\varphi\rangle$  and shifts including core relaxation  $\delta\epsilon$  are given in the following columns. The values in the seventh column correspond to the addition of fitted  $\Sigma^{(2)}$  (for E119, fitting factors from Fr are used) to the relativistic Hartree-Fock equations; the shift is found from the difference in energies when the self-energy is included and excluded. In the final column the results of Thierfelder and Schwerdtfeger [22] are presented for comparison with our core-relaxed results  $\delta\epsilon$ . The numbers in square brackets [] denote powers of 10. Units: a.u.

Atom	State	$\epsilon_{\text{exp}}^{\text{a}}$	$\epsilon_{\text{HF}}$	$\delta\epsilon^{(1)}$	$\delta\epsilon$	$\delta\epsilon_{\text{Br,fit}}$	Other <sup>b</sup>
Na	$3s_{1/2}$	-0.188858	-0.182033	1.068[-5]	1.125[-5]	1.275[-5]	1.118[-5]
	$3p_{1/2}$	-0.111600	-0.109490	-5.698[-8]	-7.088[-7]	-8.162[-7]	
	$3p_{3/2}$	-0.111521	-0.109417	1.112[-7]	-4.882[-7]	-5.629[-7]	
	$3d_{3/2}$	-0.055936	-0.055667	-2.644[-9]	4.085[-11]	1.145[-10]	
	$3d_{5/2}$	-0.055936	-0.055667	1.770[-9]	3.407[-9]	3.546[-9]	
K	$4s_{1/2}$	-0.159516	-0.147491	1.845[-5]	1.974[-5]	2.543[-5]	2.013[-5]
	$4p_{1/2}$	-0.100352	-0.095713	-1.023[-7]	-1.400[-6]	-1.805[-6]	
	$4p_{3/2}$	-0.100089	-0.095498	3.072[-7]	-8.411[-7]	-1.078[-6]	
	$3d_{3/2}$	-0.061387	-0.058067	-1.915[-8]	-2.568[-7]	-7.483[-7]	
	$3d_{5/2}$	-0.061397	-0.058080	1.382[-8]	-2.647[-7]	-7.479[-7]	
Rb	$5s_{1/2}$	-0.153507	-0.139291	4.836[-5]	5.136[-5]	6.801[-5]	5.299[-5]
	$5p_{1/2}$	-0.096193	-0.090816	1.381[-8]	-2.854[-6]	-3.806[-6]	
	$5p_{3/2}$	-0.095110	-0.089986	1.316[-6]	-1.083[-6]	-1.378[-6]	
	$4d_{3/2}$	-0.065316	-0.059687	-1.098[-7]	-1.791[-6]	-4.355[-6]	
	$4d_{5/2}$	-0.065318	-0.059745	1.005[-7]	-1.790[-6]	-4.181[-6]	
Cs	$6s_{1/2}$	-0.143098	-0.127368	8.128[-5]	8.431[-5]	1.152[-4]	8.735[-5]
	$6p_{1/2}$	-0.092166	-0.085616	1.077[-6]	-3.831[-6]	-5.355[-6]	
	$6p_{3/2}$	-0.089642	-0.083785	3.183[-6]	-9.203[-7]	-1.093[-6]	
	$5d_{3/2}$	-0.077035	-0.064420	-6.066[-7]	-1.212[-5]	-2.681[-5]	
	$5d_{5/2}$	-0.076590	-0.064530	7.174[-7]	-1.115[-5]	-2.350[-5]	
Fr	$7s_{1/2}$	-0.149670	-0.131076	2.201[-4]	2.166[-4]	2.825[-4]	2.301[-4]
	$7p_{1/2}$	-0.093913	-0.085911	1.068[-5]	1.276[-9]	1.959[-7]	
	$7p_{3/2}$	-0.086228	-0.080443	1.034[-5]	-5.888[-8]	4.849[-7]	
	$6d_{3/2}$	-0.075722	-0.062993	-8.046[-7]	-2.668[-5]	-5.991[-5]	
	$6d_{5/2}$	-0.074812	-0.063444	1.968[-6]	-2.247[-5]	-4.528[-5]	
E119	$8s_{1/2}$	-	-0.152842	7.196[-4]	6.832[-4]	7.526[-4]	7.728[-4]
	$8p_{1/2}$	-	-0.091697	7.204[-5]	5.217[-5]	8.625[-5]	
	$8p_{3/2}$	-	-0.075972	2.697[-5]	-2.001[-6]	-1.766[-6]	
	$7d_{3/2}$	-	-0.061414	4.523[-7]	-4.069[-5]	-1.068[-4]	
	$7d_{5/2}$	-	-0.063000	4.717[-6]	-3.086[-5]	-6.009[-5]	

<sup>a</sup> Data from NIST, Ref. [47].

<sup>b</sup> Thierfelder and Schwerdtfeger [22], first-order perturbative treatment of the radiative potential in the relativistic Hartree-Fock approximation.

into the potential in Ref. [22] which brings about a non-orthogonality of the wave functions with different principal quantum number  $n$ ; the level of error introduced through such non-orthogonality may be small, though should be checked when used in many-body methods.

Fitting the radiative potential to the self-energy shifts of individual hydrogen-like ions, rather than fitting over the range  $10 \leq Z \leq 120$  simultaneously, could help improve the accuracy for a specific atom or ion under consideration. This would be the case, in particular, for those atoms or ions on the lighter or heavier sides of the

range or those with lower principal quantum number  $n$ , where the current deviations from the exact self-energy calculations for hydrogen-like ions are largest.

We should stress that the physical shift is the Lamb shift, well-approximated by the one-loop self-energy and vacuum polarization shifts. Typically, the self-energy shift is an order of magnitude larger than the vacuum polarization shift and is of opposite sign. We have noticed a steeper increase of the vacuum polarization shifts [30] compared to the self-energy shifts with  $Z$ . There is a significant cancellation between the self-energy

and Uehling contributions to the Lamb shift for the  $8s$  and  $8p_{1/2}$  levels. For the  $8s$  shift, the self-energy contributes  $7.526 \times 10^{-4}$  a.u. and the Uehling potential  $-4.484 \times 10^{-4}$  a.u., respectively. For the  $8p_{1/2}$  shift, they contribute  $8.625 \times 10^{-5}$  a.u. and  $-7.643 \times 10^{-5}$  a.u. (These values are taken from Table IV of Ref. [30] and from Table VI of the current work.) This may lead to a suppression of the physical shift for these levels.

There are other contributions that will need to be considered for a more accurate description of the Lamb shift, including account of electron screening (see Section III A), higher-orders in  $Z\alpha$  vacuum polarization (Wichmann-Kroll), and higher-order loops.

Uncertainties in *ab initio* calculations of transition frequencies in alkali atoms are at the level of 0.1% [40], roughly the level where the Lamb shifts enter. The accuracy is limited by the incomplete account of electron-electron correlations. If the theoretical uncertainty can be reduced, then high-precision atomic studies of transition frequencies, particularly involving  $d$  levels, could provide a sensitive test of combined many-body and QED effects [30].

## VII. CONCLUSION

In this work we have studied the Flambaum-Ginges radiative potential method in detail. By calculating the

self-energy shifts in frozen atomic potentials and comparing with the results of exact QED, we have shown that the accuracy of the method is high and comparable to that of the Shabaev-Tupitsyn-Yerokhin model operator approach [27].

We have applied the radiative potential to the spectra of the series of alkali atoms Na through to E119. We have demonstrated, through account of core relaxation and valence-core electron correlations, that consideration of many-body effects is crucial for determining the correct sign and size of the shift for orbitals with  $l > 0$  and for obtaining high accuracy for  $s$  waves.

Generally, the effect of the many-body corrections is to increase the size of the self-energy shifts. Remarkably, the many-body enhancement is so large for the  $d$ -wave shifts that they approach the size of the shifts for  $s$  waves. High-precision atomic spectroscopic studies could provide a sensitive test of combined many-body and QED effects.

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